Branching Ratio and L2+L3 Intensities of 3d-Transition Metals in Phthalocyanines and the Amine Complexes (STATES AND STRUCTURES-Crystal Information Analysis)

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Masanori Koshino, Hideki Kurata, Seiji Isoda and Takashi Kobayashi

$L_{2,3}$ inner-shell excitation spectra were obtained by electron energy-loss spectroscopy (EELS) for the divalent first transition series metals in phthalocyanine complexes. It was found that the value of normalized total intensity of I(L_2+L_3) was nearly proportional to the formal electron vacancies of each 3d-state, and the values of the branching ratio, I(L_3)/I((L_2+L_3), represented a high spin state rather than low spin state. EELS was also applied to charge-transfer complexes of FePc with amine. It was concluded that their I(L_2+L_3) intensity of Fe showed the decrease in vacancies of 3d-states on the formation of the charge transfer complex, which suggests some electron transfer from the amine to Fe in phthalocyanine.

Keywords: Electron energy-loss spectroscopy/ Transition metals/ Phthalocyanines/ Charge transfer

For the 3d-transition metal atoms with open shell structures, characteristics of such metal compound predominately depend on its d-electronic states which contribute to the chemical bonding and also are affected easily by surrounding atoms. Electron energy-loss spectroscopy (EELS) can be used to get information on the d-states even from a small region of a specimen. Like other optical analytical methods, the $L_{2,3}$ spectra which can be obtained as a result of an excitation, for example, from the initial states $2p^6 3d^n$ to the final states $2p^5 3d^{n+1}$ will be available to investigate d-occupancy and other d-electronic states. In the present study, we examined relation between 3d-occupancy and L-edge spectra of phthalocyanines (Pc) with various 3d-metals. We also examined the spectral changes in FePc due to complex formation with gas phase amines such as pyridine or γ-picoline, where the amines are expected to act as electron donors. The branching ratio I(L_3)/I(L_2+L_3), which depends on both the valence band spin-orbit coupling and the electrostatic interactions between core-hole and valence-electron, was also obtained in each complex and compared to the calculated values on metal oxides by Thole and Laan [1].

The normalized spectra of TiOPc, CrPc, MnPc, FePc, CoPc, NiPc and CuPc are shown in Fig.1. L_2+L_3 integral intensities were measured on each spectrum in Fig.1 and plotted against the number of formal 3d-electrons as shown in Fig.2. The result reveals that the increases in d-electrons causes the decrease of L_2+L_3 intensities; that is, the metal phthalocyanines with larger number of 3d-electrons show lower L_2+L_3 intensities. It is due to the decrease in the number of vacancies in 3d-orbitals.

Relative L_3 intensities in the excitation, the branching

STATES AND STRUCTURES — Crystal Information Analysis —

Scope of research

Structures of materials and their structural transition associated with chemical reactions are studied through the direct observation of atomic or molecular imaging by high resolution spectro-microscopy. It aims to explore new methods for imaging with high resolution and for obtaining more detailed chemical information. The following subjects are studied: direct structure analysis of ultrafine crystallites and ultrathin films, crystal growth and adsorption states of organic materials, and development on high resolution energy filtered imaging as well as electron energy-loss spectroscopy.

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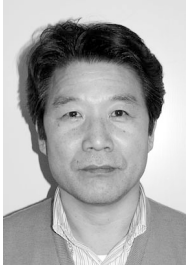

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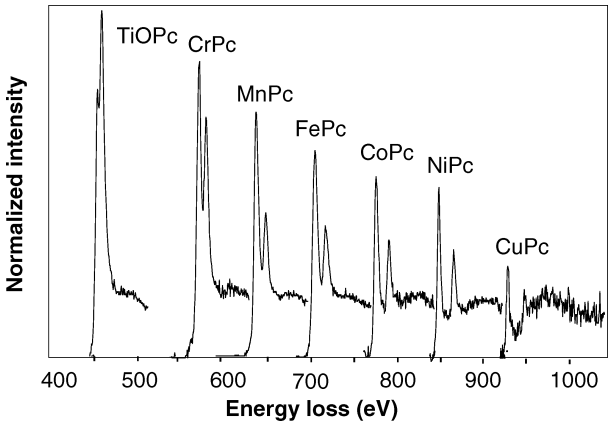

Figure 1. Series EELS spectra of MPc.

ratio $I(L_3)/I(L_2+L_3)$ is sensitive to the spin-states of 3d-electrons and shows large value for high spin-state and vice versa [2-4]. The correlation between formal 3d-occupancy and the branching ratio is shown in Fig.3 with the open circles of the line (a). These values are gradually increasing to reach the highest one of 0.72 for MnPc which has d^5 electrons and then decreasing slightly with increasing further the number of 3d-electrons. In the absence of both the electrostatic interactions between core-hole and 3d-electron and the spin-orbit coupling in the valence electrons, the branching ratio is 2/3. Actually, however, the branching ratio varies depending on spin-orbital and electrostatic interactions as well as on ligand field. Laan *et. al*. have calculated the branching ratio relating to the transition from the initial state $2p^6 3d^n$ to the final state $2p^5 3d^{n+1}$ in the series of 3d-metal ions [2]. In the figure, the calculated branching ratios for high- and low-spin states were obtained for the case when all spin-orbital split levels of

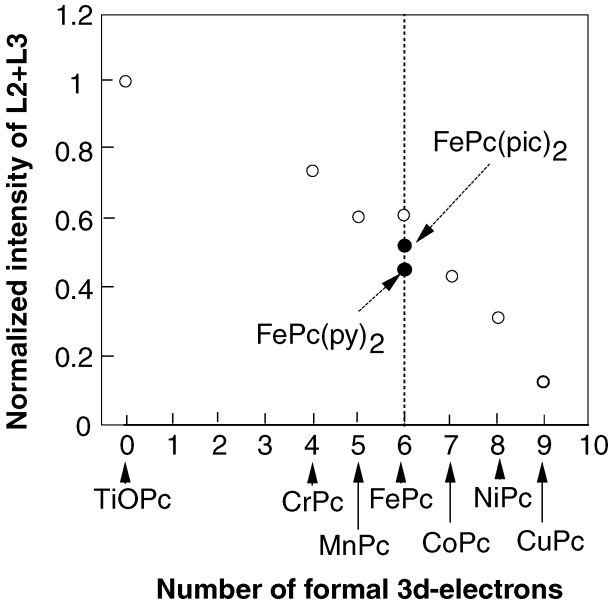

Figure 2. Normalized total intensities of L_2+L_3 as a function of the number of formal 3d-electrons.

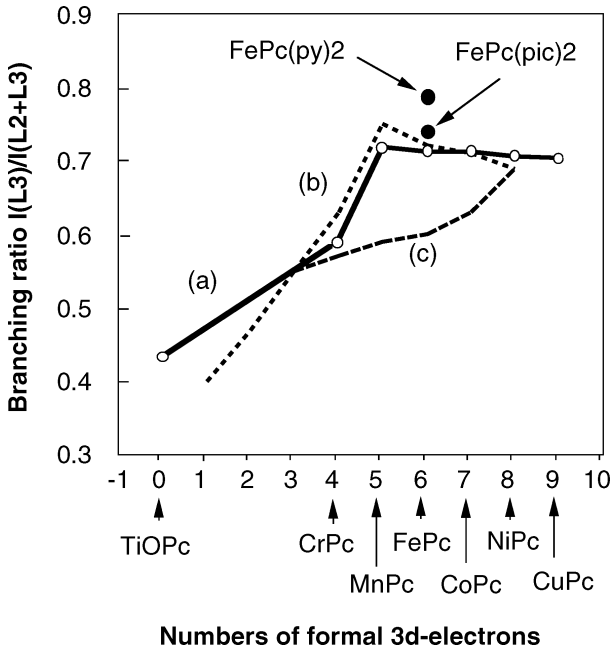

Figure 3. Branching ratio against number of formal 3d-electrons; (a) measured branching ratios of metal phthalocyanines, (b) calculated for high spin-state and (c) for low spin-state

the ground state term are equally populated (z=0, in their notation), which are represented by the curves (b) and (c) in Fig.3, respectively. The present results on MnPc, FePc and CoPc, agree well with those of the calculated ones for high-spin state. This indicates that the metal phthalocyanines from MnPc to CoPc has high spin state.

FePc-amine complexes show smaller intensity of L_2+L_3 compared to that of pristine FePc as already summarized in Fig.2, which suggests that the addition of amine ligands leads to the decrease in vacancy of 3d-states of Fe atom; that is, the amines donate some amount of electrons to Fe in FePc. In the normalized intensities of L_2+L_3 in Fig.2, the pyridine seems to donate more electrons to FePc than γ-picoline. As for the branching ratio, the amine complexes have larger values than that of FePc (Fig.3), which suggests that the spin-orbit coupling may be changed by addition of amine ligands. Here we can conclude that the amines affect not only the population of electrons, but also on the electronic interaction in FePc.

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